RPP-30993-FP
Revision 0

Fractional Crystallization of Hanford Single-Shell Tank Wastes

A Modeling Approach

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
Hanford Group, Inc.
P.O. Box 1500
Richland, Washington

RPP-30993-FP
Revision 0

Fractional Crystallization of Hanford Single-Shell Tank Wastes

A Modeling Approach

D. J. Geniesse
E. A. Nelson
AREVA NC, Inc.

D. W. Hamilton
CH2M HILL Hanford Group, Inc.

Date Published
December 2006

To Be Presented at
Waste Management 2007

Waste Management Symposia, Inc.
Tucson, Arizona

February 25 to March 1, 2007

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
Hanford Group, Inc.
P.O. Box 1500
Richland, Washington

J. D. Aardal 12/21/2006
Release Approval Date

Approved for Public Release; Further Dissemination Unlimited

WM'07
Topic Number 3.5
Eric A. Nelson
AREVA NC Inc.
509-373-2692 – Telephone
509-372-3169 – Fax
EANelson@cogema-eng.com

FRACTIONAL CRYSTALLIZATION OF HANFORD SINGLE-SHELL TANK WASTES A MODELING APPROACH

E. A. NELSON – AREVA NC INC.
D. J. GENIESSE – AREVA NC INC.
D. W. HAMILTON – CH2M HILL HANFORD GROUP, INC.

The Hanford site has 149 underground single-shell tanks (SST) storing mostly soluble, multi-salt, mixed wastes resulting from Cold War era weapons material production. These wastes must be retrieved and the salts immobilized before the tanks can be closed to comply with an overall site closure consent order entered into by the U.S. Department of Energy (DOE), the Environmental Protection Agency, and Washington State. Water will be used to retrieve the wastes and the resulting solution will be pumped to the proposed treatment process where a high curie (primarily ^{137}Cs) waste fraction will be separated from the other waste constituents. The separated waste streams will then be vitrified to allow for safe storage as an immobilized high level waste, or low level waste, borosilicate glass.

Fractional crystallization, a common unit operation for production of industrial chemicals and pharmaceuticals, was proposed as the method to separate the salt wastes; it works by evaporating excess water until the solubilities of various species in the solution are exceeded (the solubility of a particular species depends on its concentration, temperature of the solution, and the presence of other ionic species in the solution). By establishing the proper conditions, selected pure salts can be crystallized and separated from the radioactive liquid phase.

Since the Hanford wastes contain many different ions competing for solubility (dominant ones are Na^{+1}, NO_3^{-1}, CO_3^{-2}, and SO_4^{-2}) a thermodynamic modeling tool was used to determine conditions for maximum salt removal. The modeling program is commercially available software operating on a database compiled from years of chemical analyses of the SST contents. Throughout the early stages of the project the model has been used extensively to develop and guide laboratory experiments by generating evaporation surveys to determine optimum crystallization temperatures and extent of evaporation for simulants and the actual waste. In addition to planning the laboratory experiments, the model was also used to reconcile actual waste analyses data (to ensure all ions were accounted for), perform REDOX surveys (to determine oxidation states of the major dissolved ions), and develop preliminary flowsheets for the planned pilot scale and proposed production scale fractional crystallization processes.

The laboratory experiments, guided by model predictions, began with crystallizing simple salt solutions, progressed to a well characterized non-radioactive simulant, and culminated in actual radioactive waste testing. Throughout the testing program the model predictions and the

WM'07
Topic Number 3.5
Eric A. Nelson
AREVA NC Inc.
509-373-2692 – Telephone
509-372-3169 – Fax
EANelson@cogema-eng.com

experimental results were in very close agreement for sodium salt removal and extent of radioactive decontamination for the incoming feed (non-radioactive cesium was used for the simulant studies).

Developing an accurate thermodynamic model of anticipated liquid waste streams will allow decision makers to determine if fractional crystallization is a potential pretreatment option for other DOE sites. Once the model is developed, it can be used effectively for studying the effects of varying waste feed compositions without the necessity of performing an extensive laboratory experimental program.